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The main objectives of this project are to develop novel instrumentation and to understand bond breaking and formation on semiconductor surfaces. The approaches used in achieving these objectives are to determine the dependence of adsorption on the translational and vibrational energies of incident molecules and to investigate energy exchange at surfaces. The systems which have been investigated in detail are the dissociative adsorption of carbon dioxide and the nondissociative adsorption of ethane on silicon surface. For these experiments a unique differentially pumped, time-resolved spectrometer, a molecular beamline, and a ultrahigh vacuum chamber with surface instrumentation were designed and constructed.

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Report #4

HIGH TRANSLATIONAL ENERGY INDUCED REACTIONS IN SEMICONDUCTORS

Grant No. AFOSR-88-0335

Task 2306/B1, 2303/A2

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# HIGH TRANSLATIONAL ENERGY INDUCED REACTIONS IN SEMICONDUCTORS

## Objectives:

The main objectives of this project are to develop novel instrumentation and to understand bond breaking and formation on semiconductor surfaces.

## Approaches:

The approaches used in achieving the above objectives are to determine the dependence of adsorption on the translational and vibrational energies of the incident molecules and to investigate energy exchange at surfaces.

## Systems Investigated:

The systems which we have studied in detail are the dissociative adsorption of  $\text{CO}_2$  and the nondissociative adsorption of  $\text{C}_2\text{H}_6$  on the  $\text{Si}(111)7\times 7$  surface at 67-90 K.

## Instrumentation Development:

In order to carry out effectively the AFOSR supported project, a unique differentially pumped, time-resolved electron energy loss spectrometer, a molecular beamline, and a ultrahigh vacuum chamber with a combination of surface probes were designed, constructed, and put into commission.

## Summary of Research:

Extensive instrumentation development was carried out in order to perform the type of experiments set out in the AFOSR supported project. This development was necessary since the required instrumentation are not commercially available.

The ultrahigh vacuum apparatus contains facilities for sample preparation and characterization. In addition, a supersonic molecular beamline was interfaced to the differentially pumped, time-resolved electron energy loss spectrometer (TREELS). There are two unique

features about the TREELS (the only one there is!) First, it is differentially pumped, which allows the spectrometer to be operated with pressures as high as  $10^{-5}$  Torr in the electron scattering region. This operating pressure is 4 to 5 orders of magnitude higher than other spectrometers. Second, there is a multichannel detector in the analyzer (effectively 220 channels) which allows fast data acquisition. Thus it is possible to perform in-situ vibrational spectroscopy by electron scattering while the molecules from the molecular beam are impinging on the surface. The alumina nozzle can be heated to approximately 1800 K. This allows us to vary the translational energy and the vibrational populations of the incident molecules. The beam from the nozzle is chopped by the chopper and the drift time of the molecules to the mass spectrometer (QMS) downstream is measured to determine the translational energy of the molecules. The molecular beam and the electron beam intersect at the sample. The sample can be translated from this position to the upper chamber in order to be cleaned by ion sputtering and characterized by thermal desorption spectroscopy and Auger electron spectroscopy. This apparatus is very well suited for in-situ monitoring of the evolution of the adsorbed species during the interaction of gas molecules with the surface.

Two systems were extensively studied:  $\text{CO}_2$  dissociation on  $\text{Si}(111)7\times7$  at 85 K and  $\text{C}_2\text{H}_6$  nondissociative sticking of  $\text{C}_2\text{H}_6$  on  $\text{Si}(111)7\times7$  at 67-90 K. Several conclusions can be drawn from the results on  $\text{CO}_2$  dissociation. First, the sticking probability scales with the normal component of the translational energy, i.e. the data points for the different angles of incidence fall on the same curve when plotted against the normal component of the translational energy. This normal energy scaling is obeyed at both 300 K and 1000 K nozzle temperatures. Second, the sticking probability is appreciably higher at 1000 K than at 300 K for normal component of the translational energy less than about 0.8 eV. This enhancement indicates that vibrational energy plays an important role in overcoming the barrier to chemisorption. However, when the translational energy is high enough, the barrier can be overcome by the translational energy alone, and the vibrational

energy no longer affect the sticking coefficient. The sticking probability we are measuring corresponds to the dissociation of  $\text{CO}_2$  into  $\text{CO}$  and  $\text{O}$  on the surface. There are several reasons for choosing  $\text{CO}_2$ . First,  $\text{CO}_2$  is inert towards Si for  $\text{CO}_2$  impinging the surface from the ambient with translational energy given by the Boltzmann distribution for a room temperature ideal gas, i.e.  $\text{CO}_2$  does not react when you leak the gas into the chamber through a leak valve. Second,  $\text{CO}_2$  is a triatomic molecule and thus possesses different vibrational modes in contrast to a single vibrational mode for a diatomic molecule. It is then possible to investigate whether one vibrational mode is more effective than another in overcoming the activation barrier for dissociative chemisorption. We are not able to come to a definitive conclusion regarding this point from the present data. Third,  $\text{CO}_2$  leads to oxidation of the Si surface. Furthermore,  $\text{CO}_2$  is also used as a feedgas in the chemical vapor deposition of diamond films. It is worth noting that this work, to the best of our knowledge, constitutes the first molecular beam study of the dissociative sticking of a molecule on a semiconductor surface, especially the investigation as a function of the translational and vibrational energies. All other such studies were performed on metal surfaces. These data provide an activation barrier  $E_a$  of approximately 0.6 eV for the dissociation of  $\text{CO}_2$  on Si. The  $\text{CO}_2$  goes from the physisorption state, overcomes the activation barrier, and falls into the chemisorption well.

The trapping probability of  $\text{C}_2\text{H}_6$  on  $\text{Si}(111)7\times7$  at 67-90 K was studied as a function of the translational energy and vibrational population of the impinging molecules. There are several conclusions which can be obtained from these results. First, the hard cube model works quite well for translational energies less than about 0.8 eV. However, the measured sticking probability is higher than that predicted by the model at higher energies. This deviation is due to multiple scattering effects, corrugation of the surface, and the neglect of internal energies in the hard cube model. Second, the sticking probability scales as the total translational energy of the incident molecules. It is found that the sticking probability does not depend on the angle of incidence, i.e. the sticking probability is the

same for the same total translational energy having different normal component of the translational energy due to different angles of incidence. Third, vibrational energy does not affect the sticking! This is revealed by the observation that all the data points for the different nozzle temperatures fall on the same curve. It is worth noting again that this constitutes the first study, to the best of our knowledge, of the nondissociative sticking of a molecule on a semiconductor surface as a function of the translational and internal energies of the incident molecule. The ethane molecule was chosen for this study for two reasons. First, this polyatomic molecule allows us to probe the effects of different vibrational modes on the adsorption process. Second,  $C_2H_6$  is an important molecule in the chemical vapor deposition of diamond films. Third, there are different types of bonds in  $C_2H_6$ , i.e. C-C vs. C-H bonds. It is of interest to investigate whether these two different types of bonds have different activation barriers for dissociation. We were quite surprised that there was no dissociation of the molecule up to the highest translational energy and vibrational populations we can achieve in the molecular beam. Another interesting point is that the sticking of  $C_2H_6$  on Si is classical and does not exhibit quantum behavior, as is expected for this system.

The results and experience gained during this funding period were instrumental in guiding us to propose the experiments to be performed in the coming three years. We expect to devote a larger fraction of the time in taking data than building instruments in the coming three-year period, 1992-1995, compare to the previous three-year period, 1988-1991, for which this final technical report was written.

### **Publications:**

1. P.W. Lorraine, B.D. Thoms, and W. Ho, "A differentially pumped electron-energy-loss spectrometer with multichannel detector for time-resolved studies at intermediate ambient pressures", *Rev. Sci. Instrum.* **63**, 1652 (1992).
2. P.W. Lorraine, B.D. Thoms, R.A. Machonkin, and W. Ho, "Translationally and vibrationally activated reaction of CO<sub>2</sub> on Si(111)7×7", *J. Chem. Phys.* **96**, 3285 (1992).
3. B.D. Thoms, P.W. Lorraine, and W. Ho, "A molecular beam study of ethane on Si(111)7×7: energy accommodation and trapping", *J. Chem. Phys.*, in press (1992).

### **Conference Presentations:**

1. P.W. Lorraine, B.D. Thoms, and W. Ho, "A new time resolved electron energy loss spectrometer for use at high ambient pressures," 36th American Vacuum Society Conferences, October 23-27, 1989, Boston, Massachusetts.
2. P.W. Lorraine, B.D. Thoms, and W. Ho, "Translational and vibrational activation of nitrogen dissociative adsorption on Si(111)7×7", American Physical Society Meeting, March 18-22, 1990, Cincinnati, Ohio.
3. B.D. Thoms, P.W. Lorraine, and W. Ho, "Translationally and vibrationally activated dissociative adsorption of hydrogen on Si(111)7×7", American Physical Society Meeting, March 18-22, 1990, Cincinnati, Ohio.
4. B.D. Thoms, P.W. Lorraine, and W. Ho, "A molecular beam study of ethane on Si(111)7×7: energy accommodation and trapping", American Physical Society Meeting, March 16-20, 1992, Indianapolis, Indiana.